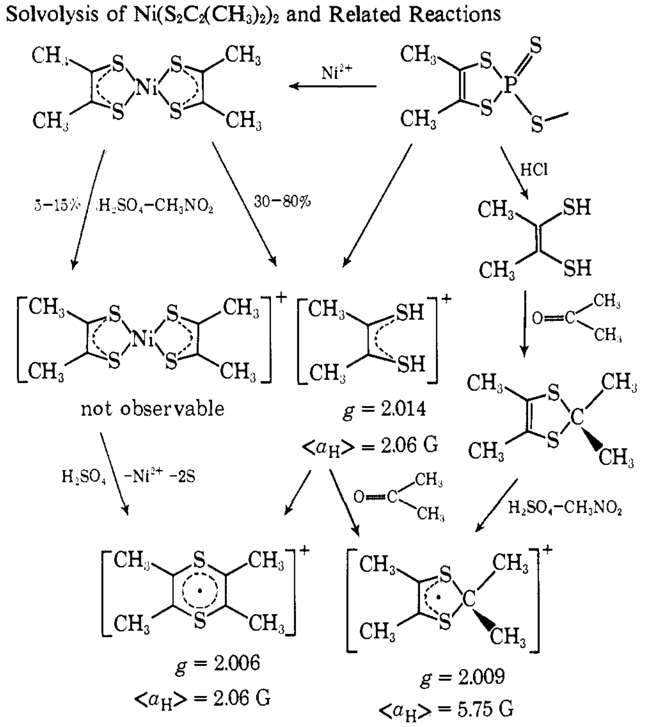
Scheme I. Formation of Radical Cations in the Oxidative Solvolysis of $Ni(S_2C_2(CH_3)_2)_2$ and Related Reactions



tronic structure of the anion $Ni(S_2C_2H_2)_2^-$, as well as the ^{33}S and ^{61}Ni esr hyperfine interaction measurements for $Ni(MNT)_2^-$ of Schmitt and Maki.[9] The ground-state electronic configuration of these anions is $^2B_{2g}$; for R = H the calculated C, S, and $Ni(3d_{xz})$ spin densities are 0.0256, 0.0969, and 0.510, respectively. The low spin density on carbon is responsible for the absence of resolved hf splitting in the esr spectra of $Ni(S_2C_2H_2)_2^-$ and the CH_3-substituted derivative. The esr signals of the radical cations 2 exhibit pronounced threefold anisotropy if examined in H_2SO_4-CH_3NO_2 glass at 100°K, which thus is partly responsible for the threefold anisotropy of the signals of the ions $M(S_2C_2R_2)_2^-$. The oxidative solvolysis of various metal trisdithienes produces esr signals of type II in 40–80 wt% H_2SO_4 in CH_3NO_2. The decomposition of $W(S_2C_2(CH_3)_2)_3$ and of $(CH_3)_2C_2S_2Ni \cdot Lig$ (Lig = $(C_6H_5)_2P$-$(CH_2)_2$-$P(C_6H_5)_2$ in 5–10% H_2SO_4-CH_3NO_2 yields a new symmetrical seven-line esr signal at $\langle g \rangle = 2.009$ with $\langle a_H \rangle = 6.1$ G, which we consider to be due to the dimethylthiirene radical cation. Work to characterize this species is in progress.

Acknowledgment. This work was supported by Grant No. 3486/A 3 of the Petroleum Research Fund, administered by the American Chemical Society, and from Institutional Grant No. GP 5208 of the National Science Foundation.

(9) R. Schmitt and A. H. Maki, *J. Amer. Chem. Soc.*, **90**, 2288 (1968).

* Address correspondence to this author.

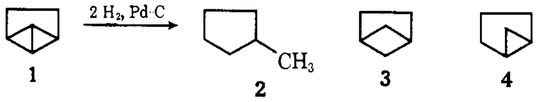
G. N. Schrauzer,* H. N. Rabinowitz
Department of Chemistry, Revelle College
University of California, San Diego, La Jolla, California 92037

Received May 8, 1970

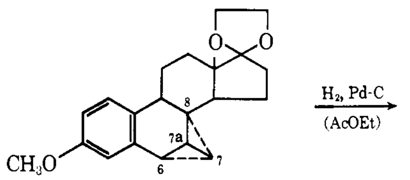
A Steroidal Bicyclobutane and Its Hydrogenolysis

Sir:

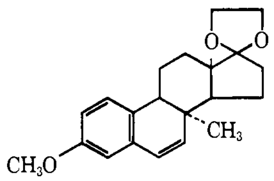
From previous studies of the hydrogenolysis of bicyclobutane systems, only tetrahydro products are known;[1,2] our picture of this reaction is thus limited by the lack of information regarding the existence and nature of dihydro intermediates. An attempt to obtain such information was made by Lemal and Shim;[3] having observed no intermediate in the reaction **1** → **2**, they proceeded to demonstrate the stability of the (independently prepared) dihydro derivatives **3** and **4** to the conditions of the reaction and could therefore exclude them as intermediates. The formation of **2** was then tentatively interpreted as involving simultaneous hydrogenolysis of two bonds.



Here we wish to report that from the hydrogenolysis of our steroidal bicyclobutane derivative **5**—itself of considerable interest[4]—a unique dihydro product, **6**, can be obtained in high (>80%) yield.[5,6]



5, mp 161–162°, $[\alpha]_D + 51.8°$



6, mp 101.5–103°, $[\alpha]_D - 31.6°$

On stirring the solution of **5** in acid-free ethyl acetate under H_2 (760 mm) with a prehydrogenated Pd–C 10% catalyst, the initially rapid gas uptake slows abruptly after 1 equiv has been absorbed (3–4 min). Work-up at this point allows **6** to be obtained. With deuterium gas, the reaction proceeds analogously and *both D atoms appear in the* 8α-*methyl group of* **6** (nmr).[7]

This, we think, is the first recognized case of what may be called *geminal hydrogenolysis* with the concomitant formation of a C=C double bond and we propose the following rationalization. The catalyst, approaching **5** from the α side, would first add one H to the most protruding (and, incidentally, most acidic—see below) site C_7 under the cleavage of bond C_6–C_7 and the development of a delocalized C_6 radical, **8**. A second H would then be delivered to the same site, accompanied by the fission of C_7–C_{7a} and the formation of the C_6–C_7

(1) For a review, see K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 186 (1968).

(2) Chemical reduction to cyclobutanes has recently been described: W. R. Moore, S. S. Hall, and C. Largman, *Tetrahedron Lett.*, 4353 (1969).

(3) D. M. Lemal and K. S. Shim, *ibid.*, 3231 (1964).

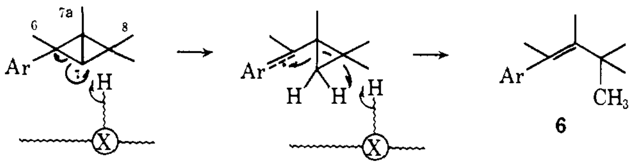
(4) This is the second example of a bicyclobutane built into a steroidal skeleton; for the first one, see W. G. Dauben and F. G. Willey, *ibid.*, 893 (1962); W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

(5) Satisfactory elementary analyses, ir, uv, nmr, and low-resolution mass spectra were obtained for each compound discussed.

(6) By direct crystallization.

(7) The three-proton singlet corresponding to the 8α-CH_3 in **6** (0.87 ppm, $CDCl_3$) becomes a broad one-proton peak (half-height width, 3 cps) in **6**-d_2; the two-proton AB pattern corresponding to the olefinic protons in **6** reappears in **6**-d_2 at full intensity.

double bond. Steric factors render hydrogenation at site C_6 (or of the new double bond) noncompetetive.[8a]



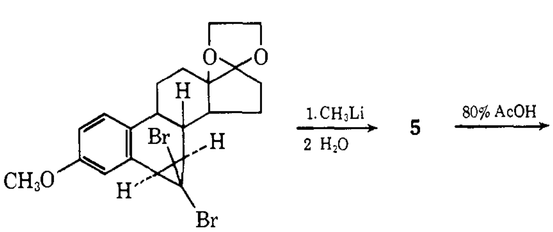
7

8

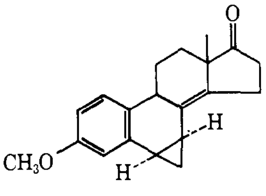
6

While the formation of **6** in high yield is undoubtedly due to an interplay of special electronic and steric factors, dihydro intermediates of this type may well play a role in the hydrogenolysis of simpler bicyclobutanes like **1**—at least one cannot exclude them on the basis of available experimental evidence.

We have prepared **5** from **9**[9] with 1.7 *M* ethereal CH_3Li solution (−70° → 25°, ice quenching) in 56% yield.[6] Undoubtedly, this reaction involves—analogously to established simpler cases[10]—insertion of an incipient carbene into the only available C–H bond for an intramolecular process, namely that at 8β.[11,12] The structure **5** is supported by, *e.g.*, the 22.63-Mcps ^{13}C nmr spectrum:[13] signals appear at 183.5 and 184.0 ppm with $J_{^{13}C^1H} = 200 \pm 20$ cps (C_7, C_{7a})[14] and at 172.3 ppm; this latter signal remains a singlet in the partially undecoupled mode, designating therefore a quaternary carbon at an unusually high field, *i.e.*, C_8.



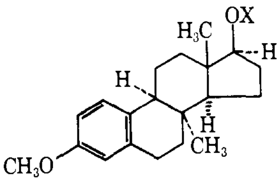
9, mp 199–200°, $[\alpha]_D$ −80.4°



10, mp 98–104°

As a bicyclobutane built into an asymmetric environment, **5** shows other interesting reactions. In agreement with the tendency of bicyclobutanes to anion formation,[15] **5** can also be metalated (*n*-BuLi, "Dabco," hexane, 25°, 8 hr).[16] It is noteworthy that the charge rests predominantly, if not exclusively, at C_7 (rather than being distributed between C_7 and C_{7a}), as shown by the finding that the **5**-*d* obtained on D_2O quenching gives on subsequent hydrogenolysis a **6**-*d* in which 95 ± 5% of the deuterium appears in the 8α-CH_3 group (nmr).[17] Not unexpected is the great sensitivity of **5** toward protons or electrophiles in general; with 80% AcOH at 25°, it is converted into a product to which—in consideration also of what is known of bicyclobutane solvolysis[18]—we assign, tentatively,[19] structure **10**.

Our structural assignments fulfill the requirement that all chemical and spectral observations fit into a reasonable and self-consistent picture.[5] Furthermore, **6**, by more vigorous hydrogenation (Pd–C, EtOH, 70°) and modification of the functionality at C_{17}, could be converted into **11**, which then was directly compared (and found not to be identical) with the authentic 8β-CH_3,[20] 9α-CH_3,[21] and 9β-CH_3[21] analogs. The definite



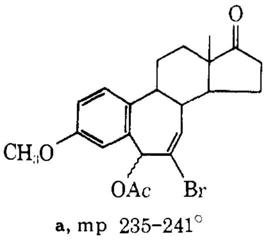
11, X = H; mp 142–143°; $[\alpha]_D$ + 46.5°

12, Δ^6, X = $COCH_2Br$; mp 147–148° $[\alpha]_D$ − 14.4°

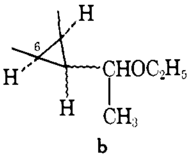
---

[8] (a) This statement is supported by the X-ray analysis[8b] of **12**. The closeness of atoms C_7 and C_{18}, in the solid state (3.2 Å), to the extent it is duplicated in solution, precludes hydrogenation of the Δ_6 double bond from the β side. (b) H. P. Weber, private communication.

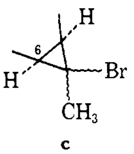
[9] Obtained from the corresponding olefin by the addition of dibromocarbene, generated from $PhHgCBr_3$ in boiling cyclohexane (see *e.g.*, D. Seyferth, *et al.*, *J. Amer. Chem. Soc.*, 87, 4259 (1965)). Both α and β adducts were isolated. The α configuration was assigned to the lower melting (mp 177–180°, $[\alpha]_D$ −67.6°) isomer, showing in nmr the characteristic 6-H doublet (J = 10 cps) at a lower field than **9** (δ 2.89 *vs.* 2.59 ppm, $CDCl_3$); models indicate that the 6C–H bond is in the plane of the aromatic ring in the case of the α and out of plane (~45°) in the β adduct. Further support to this assignment may be seen in the readiness by which the α adduct (and not the β adduct) undergoes Ag^+-assisted acetolysis; again according to models, the departure of the *endo*-Br (*cf.* S. J. Cristol, R. M. Seguiera, and C. H. DePuy, *J. Amer. Chem. Soc.*, **87**, 4007 (1965); P. v. R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *ibid.*, **88**, 2826 (1966)) should be sterically accelerated with the α adduct (9α-H!) but not with the β adduct. Solvolysis of the former with 1 mol of AgOAc in boiling AcOH is complete in 2 hr, the product being mostly **a**, as shown by its conversion through hydrogenolysis to B-homoestrone methyl ether (*cf.* E. Galantay and H. P. Weber, *Experientia*, **25**, 571 (1969)). **9** is only deketalized under the acetolysis conditions.



a, mp 235–241°



b



c

[10] W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961); see also ref 1 and 2.

[11] Side products isolated from this reaction are the sterically nonhomogeneous carbene–solvent insertion product **b** (30%) and the coupling product **c**. See ref 9 and E. T. Marquis and P. D. Gardner, *Tetrahedron Lett.*, 2793 (1966).

[12] From the reaction of the α-dibromomethylene isomer of **9** with CH_3Li, no self-insertion product could be isolated, the main product being a dimer $C_{44}H_{52}O_6$, mp 277°. Compare W. R. Moore and W. R. Moser, *J. Org. Chem.*, **35**, 908 (1970).

[13] Courtesy of the Bruker Co. Spectra were taken on an HX-90 spectrometer with pulse equipment; in $CHCl_3$; chemical shifts are upfield from CS_2.

[14] See ref 1, pp 193 ff.

[15] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 2022 (1963); G. L. Closs and R. B. Larrabee, *Tetrahedron Lett.*, 287 (1965).

[16] Conditions by J. R. Edman, *J. Amer. Chem. Soc.*, **91**, 7103 (1969). D_2O quenching of the CH_3Li reaction mixture in the preparation of **5** does not give **5**-*d*.

[17] The three-proton singlet of **6** at 0.87 ppm ($CDCl_3$) appears as a broader (half-height width 2.6 cps) two-proton peak in **6**-*d*; the olefinic region is unchanged.

[18] K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970); see also ref 4.

[19] The β configuration of the cyclopropane moiety of **10** is tentative, *i.e.*, the assumption that the proton attacks **5** at the C_{7a}–C_8, rather than at the C_7–C_8 linkage. At any rate that proton appears, expectedly,[18] as an *endo*-cyclopropane proton in **10**; in the nmr spectrum of **10**-*d*, obtained from **5** with AcOD–D_2O, the one-proton multiplet of **10** at δ −0.19 ppm is missing; the one-proton multiplet of **10** at δ 1.40 ppm becomes a triplet, J = 9 cps, in **10**-*d*.

[20] W. Nagata, *Proc. Int. Symp. Drug Res.*, *1967*, 188 (1967). We are grateful to Dr. Nagata for his supplying a sample of 8β-methylestradiol methyl ether.

[21] R. V. Coombs, J. Koletar, and E. Galantay, to be published.

structural proof of **6** (and thereby also of **5**) was given by the X-ray analysis of **12**. The crystal structure of **5** itself has not been solved so far.[8b]

It is obvious that the present findings—besides being relevant to the problem of bicyclobutane hydrogenolysis—have several other points of interest. For example, an easy access to the novel, biologically active 8α-methylestrane system is provided and the sequence exemplified by **9** → **5** → **6** → **11** offers considerable potential as a method for introducing angular methyl (or CH_3-d_{1-3}) groups. Both the scope of this method as well as further aspects of the reactivity of **5** are under active investigation.

Acknowledgment. The authors thank Dr. R. A. Coombs as well as Dr. K. Frei and his colleagues Dr. H. Lichti and Dr. P. Niklaus, for mass spectral and nmr contributions.

* Address correspondence to this author.

Eugene Galantay,* Nicholas Paolella
Sandor Barcza, Robert V. Coombs
Pharmaceutical Research, Sandoz-Wander, Inc.
Hanover, New Jersey 07936

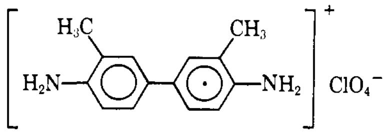
Hans Peter Weber
Physicochemical Laboratories, Pharmaceutical Division
Sandoz A.G., 4000 Basle 13, Switzerland

Received June 25, 1970

On the Electrogeneration and Characterization of a Stable, Solid, Ionic Free Radical

Sir:

We wish to report the direct electrogeneration of a stable, solid, ionic organic free radical. This entity is prepared in greater than 90% current yield by electrooxidation at a platinum anode of 3,3′-dimethyl-4,4′-diaminobiphenyl (*o*-tolidine) in methylene chloride containing tetraethylammonium perchlorate (TEAP). The blue-black electrolysis product of *o*-tolidine (*o*-T) under these conditions adheres tenaciously to the electrode surface as it is formed, yet does not "block" the electrode surface with respect to continued electrooxidation of *o*-T. The progress of the reaction is followed by spectral monitoring of the decrease of *o*-T or by the decrease in current under potentiostatic electrolysis conditions. Following exhaustive electrooxidation, the electrode product is mechanically removed from the anode. Elemental microanalysis of this material shows it to be the *o*-T analog of Wurster's Blue perchlorate, namely, I (*Anal.* Calcd for $C_{14}H_{16}N_2O_4Cl$: N, 9.00; Cl, 11.37. Found: N, 9.52; Cl, 10.77). The composition of the electrolysis product is independent of the oxidation potential from +0.5 to +0.8 V *vs.* sce.



I

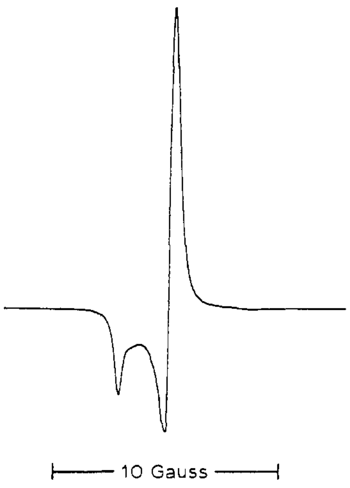
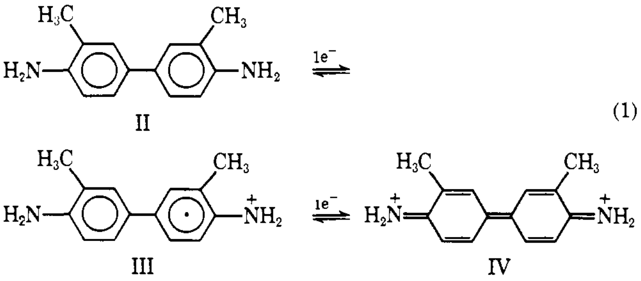


Figure 1. The esr powder spectrum of I in dry KCl; concentration is 0.32% by weight; temperature = 40°; $g_{\parallel} = 2.0037$; $g_{\perp} = 2.0021$.

The electrochemistry of *o*-T was examined in a solvent in which compound I is soluble. Thus in acetonitrile (AN) containing TEAP, cyclic voltammetry at a platinum electrode shows that *o*-T is oxidized in two steps with peak potentials of 0.5 and 0.7 V *vs.* sce. Controlled-potential coulometry shows that each of these two steps involves the heterogeneous transfer of one electron per molecule, as has been observed for *o*-T in aqueous acidic medium,[1] corresponding to the respective formation of the cation radical and diimine of *o*-T. The spectral characteristics of compounds II–IV are summarized in Table I. The hyperfine electron spin resonance (esr) spectrum of III is observed for both *in situ* and external electrooxidations of *o*-T in degassed AN containing TEAP. More than 60 lines are resolved with a total spectrum width of 38 G having $\langle g \rangle = 2.0023$.



(1)

Dissolution of the titled material (I) in AN gives rise to visible and hyperfine esr spectra which are identical with those obtained through direct electrooxidation of *o*-T in AN.

The solid-state esr spectrum of polycrystalline I in dry KCl is shown in Figure 1. The temperature dependence of this magnetic resonance spectrum of 1.0×10^{-4} *m* I in KCl is shown in Figure 2. This change in paramagnetism with temperature is analogous to that found in the case of Wurster's Blue (WB) perchlorate[2–7] with the "transition temperature" of I occurring at *ca.* 335°K as opposed to 186°K for WB perchlorate. These results suggest that a dimerization of I occurs in the solid state as reported by McConnell,

---

[1] T. Kuwana and J. W. Strojek, *Discuss. Faraday Soc.*, **45**, 134 (1968).

[2] L. Michaelis and S. Granick, *J. Amer. Chem. Soc.*, **65**, 1747 (1943).

[3] G. K. Hughes and N. S. Hush, *Proc. Roy. Soc.*, **81**, 48 (1947).

[4] K. H. Hausser and H. Kainer, *Chem. Ber.*, **86**, 1563 (1953).

[5] N. Elliot and M. Wolfsberg, *Phys. Rev.*, **91**, 435 (1955).

[6] K. H. Hausser, *Z. Naturforsch. A.*, **11**, 20 (1956).

[7] W. Duffey, Jr., *J. Chem. Phys.*, **36**, 490 (1962).